

# ***Ab Initio* Simulations of Temperature Dependent Phase Stability and Martensitic Transitions in NiTi**

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## Abstract

For NiTi based alloys, the shape memory effect is governed by a transition from a low-temperature martensite phase to a high-temperature austenite phase. Despite considerable experimental and computational work, basic questions regarding the stability of the phases and the martensitic phase transition remain unclear even for the simple case of binary, equiatomic NiTi. We perform *ab initio* molecular dynamics simulations to describe the temperature-dependent behavior of NiTi and resolve several of these outstanding issues. Structural correlation functions and finite temperature phonon spectra are evaluated to determine phase stability. In particular, we show that finite temperature, entropic effects stabilize the experimentally observed martensite (B19') and austenite (B2) phases while destabilizing the theoretically predicted (B33) phase. Free energy computations based on *ab initio* thermodynamic integration confirm these results and permit estimates of the transition temperature between the phases. In addition to the martensitic phase transition, we predict a new transition between the B33 and B19' phases. The role of defects in suppressing these phase transformations is discussed.

Shape memory alloys are materials that after deformation recover their original shape upon heating. They are technologically important for a wide range of applications, including actuators, shape-morphing wings and next generation space suits, among others. Nickel Titanium (nitinol) is perhaps the best-known example in this class of alloys and figures prominently in many commercial applications. The shape memory effect in NiTi is driven by a martensitic phase transition from a low temperature martensite phase (B19') to a high temperature austenite phase (B2).<sup>1,2</sup> Many applications involving shape memory alloys are tied to the specific value of the martensitic phase transition temperature.<sup>3</sup> Having the ability to tune this transition temperature, for example, through ternary additions in NiTi-based alloys,<sup>3-5</sup> will open the door to significantly more far-reaching applications. However, even for binary, equiatomic NiTi, which is the simplest example in this class of materials, basic questions regarding the stability of the phases and the martensitic phase transition remain unclear. In this paper, we resolve several of these important, outstanding issues.

Experimentally, the high temperature austenite phase of NiTi has the cubic B2 ( $Pm\bar{3}m$  symmetry) structure. The low temperature martensite phase has the monoclinic B19' ( $P2_1/m$  symmetry) structure, with an experimentally determined angle  $\gamma$  of  $98^\circ$ .<sup>6,7</sup> The transition temperature between the two phases is reported to be approximately 341 K.<sup>8</sup> Relevant crystal structures are shown in Figure 1. Considerable computational work has been performed to understand the phases of NiTi and related materials. In particular, density functional theory (DFT) studies<sup>9-22</sup> have provided many insights into the energetics and properties of NiTi; but they have also generated new unanswered questions. For example, DFT formation energies for B2 are in good agreement with experiments;<sup>23-26</sup> however, B2 is predicted to be dynamically unstable at  $T = 0$ , i.e. certain phonons modes have imaginary frequencies.<sup>27</sup> Recent attempts using small systems to include finite temperatures effects into B2 stability analyses have given contradictory results.<sup>28,29</sup> On the other hand, B19' at the experimental monoclinic angle  $\gamma$  of  $98^\circ$  is dynamically stable at  $T = 0$ ; however, the computed structure is unstable to shear.<sup>12</sup> Huang *et al.* determined the DFT ground state of NiTi

45 at  $T = 0$  to be a new orthorhombic phase (B33) with an angle of  $\gamma = 107.3^\circ$ .<sup>30</sup> However,  
 46 the B33 structure has not been observed experimentally in NiTi and its crystal symmetry  
 47 ( $Cmcm$ ) is incompatible with the shape memory effect, and therefore cannot represent the  
 48 martensitic phase of this material. Thus, after considerable computational analysis, we are  
 49 in the unsatisfying position that the two experimentally observed phases for NiTi have un-  
 50 determined stability; whereas the only computed stable phase has never been observed and  
 51 is incompatible with the shape memory effect.

52 To address these discrepancies, we perform high accuracy, *ab initio* molecular dynamics  
 53 (AIMD) simulations based on density functional theory combined with extended thermody-  
 54 namic integration methods to evaluate the stability and relative free energies for the defect-  
 55 free, single crystal phases (B2, B19', B33) of NiTi for a range of temperatures up to 900 K.  
 56 These materials are strongly anharmonic, and therefore, methods based primarily on phonon  
 57 analysis, even at finite temperatures, will not capture the full behavior. This necessitates  
 58 high accuracy computations of the free energy. We show that finite temperature, entropic  
 59 effects resolve many of the controversies derived from previous studies, bringing computa-  
 60 tion into much closer agreement with experiment. Specifically, we show that entropic effects  
 61 stabilize both B2 and B19' while destabilizing B33. Furthermore, the martensitic transition  
 62 temperature is estimated between these stable phases. In addition, we also identify a new  
 63 phase transition between B33 and B19'.

64 For B2, B19', and B33, we consider phase stability from several complementary view-  
 65 points. For each case, the lattice vectors of the AIMD simulation cells are optimized such  
 66 that all finite temperature components of the stress tensor are zero. This procedure not only  
 67 accounts for thermal expansion, but also places the system at a critical point on the free  
 68 energy surface. Next, we examine deviations of the crystalline structure from ideality during  
 69 the course of the simulations in these optimized cells. Structural evolution is evaluated quan-  
 70 titatively with: (1) normalized position correlation functions (NPCFs)<sup>31</sup> and (2) atomic dis-  
 71 placement scatter diagrams.<sup>32</sup> The NPCF is proportional to  $\sum_i \langle (r_i(t-t_0) - R_i^0) \cdot (r_i(t_0) - R_i^0) \rangle$

where  $r_i(t)$  are the atomic trajectories from the AIMD simulation,  $R_i^0$  is the ideal reference lattice vectors of interest and the brackets are ensemble averages. For long times ( $t \rightarrow \infty$ ), vibrational motion becomes uncorrelated, and therefore,  $\text{NPCF} \rightarrow 0$  indicates stabilization with respect to the reference lattice whereas nonzero values indicate the converse. We plot the atomic displacements explicitly relative to the reference structures on scatter diagrams. Significant deviations from zero displacement signal an instability.

Both NPCFs as well as atomic displacement scatter plots are shown in Figure 2 for 144 atom cells of B33, B19', and B2. Large cell sizes are required to eliminate finite size effects (see Supplemental Documentation for extensive convergence tests for all computed properties). Figure 2a, b, and c, shows very different behavior for the three phase at different temperatures. For B33, the NPCFs indicate structural stability at lower temperatures, 50 K and 300 K, but instability for  $T > 300$  K. Convergence times at 300 K are almost two orders of magnitude larger than at 50 K. This may indicate the proximity of a stability transition for B33. Interestingly, the B19' phase loses its  $T = 0$  non-zero shear stress even at low  $T$  and maintains its ideal configuration across the full 50 to 600 K temperature range considered. Perhaps most striking is that while the B2 structure is unstable at 50 K, it stabilizes for  $T > 300$  K. Unlike B33, the NPCF convergence rates for B2 increase with increasing temperature.

The atomic displacements scatter plots for B2, B19', and B33 are shown in the overlay plots in Figure 2a, b, and c, respectively. For each case, displacements are provided for 50 K (blue circles) and 600 K (red squares). At low temperatures, B33 displacements are negligible; however, at high temperatures, large displacements on the order of 0.5 Å can be seen in the  $a$  direction. Displacements in  $a$  result from thermally induced motion along the [100](011) stacking fault, which previously has been shown from DFT calculations to be important for the martensitic transition.<sup>9,10</sup> At low and high temperatures, the B19' phase exhibits only minor displacements,  $\sim 0.05$  Å. The B19' displacements do not show any particular ordering and can most likely be attributed to vibrational motion, as indicated

by the loss of correlation in the NPCF. The B2 phase at low temperatures shows large displacements  $\sim 0.4$  Å from ideality. At higher temperatures, however, these displacements largely vanish, as seen in the tight clustering near the origin. Both the NPCF and the atomic scatter plots indicate that for  $T > 300$  K, the high temperature phase of NiTi is very closely approximated by ideal B2.

Phase stability is further investigated by explicit computation of temperature-dependent phonons as derived from the AIMD simulations.<sup>33,34</sup> Imaginary phonon modes (represented as negative numbers) indicate the crystal structure is dynamically unstable, i.e. it is not a local minima of the energy. Phonon spectra are shown in Figure 3 at both zero-temperature and at 600 K. It is important to note that these results are very sensitive to cell size, and therefore, using sufficiently large cells is crucial to obtain reliable results. Because of this, 144 atom cells were employed for computations on all phases (see Supplemental Figures S3-S8 for convergence study results). The B33 phase, given in Figure 3a, develops imaginary modes at 600 K through the lowering of the TA mode along the  $\Gamma \rightarrow A$  direction. Phonon dispersions for the B19' phase shows stability across the full temperature range investigated, as shown in Figure 3b. Most dramatically perhaps, the imaginary modes reported for the B2  $T = 0$  K phonon dispersion lift and become positive at 300 K, as shown in Figure 3a, indicating stabilization of this phase, consistent with the structure analysis of Figure 2.

The stress tensor, structure, and phonon analyses provide a complementary picture of the temperature dependent stability of the three phases that is consistent with experiment. Namely, stable phases at a given temperature exhibit the following properties: all components of the stress tensor (normal stresses and shears) are on average zero; the NPCF goes to zero in finite time; and all phonon modes are positive. Our results therefore show that finite temperature, entropic effects stabilize the high-temperature B2 phase between 50 and 300 K. Similarly, the low-temperature B33 phase is progressively destabilized, fully losing stability between 300 K and 600 K. The B19' phase, on the other hand, is unstable to shear at  $T = 0$  but exhibits full stability from 50 K up to 700 K.

To obtain further insights into phase stability as well as transitions between the phases, we next compute the relative free energies of the phases. Vibrational entropy is frequently evaluated via the quasi-harmonic approximation (QHA). However, stability issues at  $T = 0$  invalidates this approach for B2 due to the appearance of imaginary phonon modes. Alternatively, stable, finite temperature phonon spectra can be used with the QHA expressions to obtain entropy estimates. However, for strongly anharmonic materials such as NiTi, this approach will not be a good approximation to the full anharmonic entropy. This strong anharmonicity therefore necessitates the use of high accuracy methods for computing free energies. For this reason, we use two different methods based on thermodynamic integration to compute the free energies. The computations should be exact to within the accuracy of DFT.

Our first approach is a generalization of the stress-strain methods developed previously for transition metals.<sup>35</sup> Those methods based on Bain path integration are necessarily volume conserving; however, many systems of interest including NiTi do not conserve volume between the phases. We generalized that approach to account for arbitrary volume changes in an exact way. We expect this method to have applicability beyond what is presented here. Our generalized stress-strain method requires a well defined, continuous path in lattice vector space between the two given phases. For NiTi, the monoclinic angle,  $\gamma$ , provides a natural, continuous parameter to connect the three phases of interest shown in Figure 1. In general, multiple paths can be considered; however, the B33→B19'→B2 path was determined to be the best behaved and is equivalent to motion along the  $\langle 100 \rangle \{110\}$  generalized stacking faults. Spontaneous motion along this fault was found in the high temperature B33 phase during structural stability tests. The B33→B19' path is largely a transformation in  $\gamma$ -space, as the lattice vectors are of comparable magnitude, while the B19'→B2 path involves non-trivial changes to both  $\gamma$  as well as the lattice vectors. Optimization of the simulation cells to obtain zero stress is required to ensure the obtained free energy differences, which are Helmholtz free energy differences, are equivalent to Gibbs free energy differences. We

find the internal atomic coordinates for the 144 atom cell for this path to transform continuously and that the stresses converge rapidly ( $< 10$  ps) (see Supplemental Figure S9). It should be noted that while free energy differences between stable phases can be rigorously computed, evaluation of free energies differences involving unstable structures is still an area of active investigation. Therefore, free energies involving unstable structures may contain some systematic error as discussed recently.<sup>36</sup>

Our second approach uses the Einstein crystal method to compute free energy differences at isolated points along the transformation paths. These computations were used to check the stress-strain method and were only performed at free energy minima along the transformation path. The reference harmonic free energy is obtained from the force constants associated with the temperature dependent phonon dispersions. This approach overcomes difficulties in using  $T = 0$  K phonon dispersions with imaginary modes. For each stable crystal at a given temperature, thermodynamic integration is performed from the system described by the harmonic reference potential to the one described by DFT. The integration can result in anharmonic contributions to the free energy on the order of 5 meV/atom compared to the harmonic reference free energy. This nontrivial anharmonic contribution to the free energy can shift the transition temperature by as much as 100 K and thus confirms the need for high accuracy or exact methods to study these systems.

Free energy results using the generalized stress-strain method at 0, 50, 300, and 600 K are given in Figure 4a as a function of  $\gamma$ . Einstein crystal results are shown as open symbols for validation. Agreement between the methods is excellent ( $\leq 1$  meV/atom). The  $T = 0$  curve reproduces previous DFT results, and clearly shows that B2 and B19' are not energetic minima whereas B33 is a stable minimum, as reported by Huang *et al.*<sup>30</sup> We see however that the free energy surface changes considerably as a function of temperature. Between B33 and B19', a small but distinguishable barrier develops between the phases for  $T = 50\text{K} - 300\text{K}$ . Above 600 K, however, the free energy is monotonically decreasing from B33 to B19'. Importantly, B19' develops a clearly defined free energy minima above 50 K. Thus,



B19' is entropically stabilized and develops into a separate phase distinct from B33. The B2 phase is unstable to transitions to B19' until 300 K, above which a free energy barrier develops stabilizing this phase as a local minima. These results are consistent with the structural and phonon analysis.

Further detail is provided by Figure 4b where free energy differences relative to the most stable phase are mapped as a function of  $T$  and  $\gamma$ . Blue and red represent small and large free energy differences, respectively. The free energies are again derived from the generalized stress-strain method. The free energy map illustrates the stability regions associated with each of the phases: B33, B19', and B2. White circles indicate stable points of each phase, i.e. all finite temperature stresses are zero and all finite temperature phonons are real and positive. Thus each white circle represents a stable, free energy minimum for that phase and the white lines denote the extent of the stable free energy basins. Free energy and stability results are provided for 50 K as well as between 0 and 900 K in steps of 100 K. The regions of stability for each phase are found to be  $0 < T < 300$  K for B33,  $50 < T < 600$  K for B19', and  $T > 300$  K for B2. Interestingly, the B19' angle is shown to be a function of temperature, ranging from  $\sim 100^\circ$  at 50 K to  $\sim 98^\circ$  at 600 K. Furthermore, the stable basin of B19' is relatively shallow suggesting that  $\gamma$  values for this phase might be fairly sensitive to small changes in stress. This could be important since stress fields associated with defects could potentially alter the value of  $\gamma$  quoted here. The free energy results allow us to estimate the phase transition temperatures. In particular from Figure 4, the transition between B33 and B19' appears to occur between 50 and 300 K. The B19'  $\rightarrow$  B2 free energy path, is uphill until 600 K, indicating that a transition occurs between 300 and 600 K.

Differences in the Gibb's free energy ( $\Delta G$ ) between the various stable phases as a function of  $T$  are plotted in Figure 5. Vanishing of the free energy difference indicates a phase transition. For  $\Delta G$  between B33 and B19', a new phase transition is predicted to occur at  $75 \pm 26$  K. For B19' to B2,  $\Delta G$  goes to zero at  $500 \pm 14$  K. The larger error for the low- $T$  transition is a function of the slope of  $\Delta G$  and the target accuracy of 1 meV/atom.

The low values for the B33→B19' transition temperature explains the lack of experimental evidence for B33, despite being energetically favored at 0 K. If B33 becomes unstable at low temperatures, it may be difficult to synthesize and therefore to observe. The B19'→B2 transition temperature is roughly 150 K above the experimental value of 341 K.<sup>8</sup> However, the methods used to obtain this value, based on *ab initio* thermodynamic integration, are numerically exact to within the accuracy of DFT. Therefore, we expect it to be a reliable estimate of the martensitic transition temperature for defect-free, single crystal NiTi. The non-trivial difference with experimental values is most likely due to defects that have been shown to suppress transition temperatures in this and related materials.<sup>37</sup> This also suggests that improved processing resulting in higher material quality could produce materials with higher measured transition temperatures. In addition, it is also known that the transition temperature is dependent on the heating and cooling rates with slower rates giving higher transition temperatures. Since we use equilibrium methods to estimate this temperature, our results correspond effectively to infinitely slow rates. For that reason, we expect them to be an upper bound for the experimental transition temperature.

We have performed a comprehensive computational analysis based on *ab initio* molecular dynamics of the stability and transitions between the major phases of NiTi: B2, B19', and B33. Considerable previous computational analysis based mainly on  $T = 0$  DFT resulted in significant discrepancies between experiment and computation. We have shown that by including temperature dependent entropic effects into the computations, many of these differences can be resolved. We show that B2 and B19' are stabilized due to these entropic effects whereas B33 is destabilized. These materials are shown to be highly anharmonic. Anharmonic contributions to the free energy can shift the transition temperature by as much as 100K and thus necessitates the need for high accuracy or exact methods to study these systems. We develop an generalized stress-strain method to perform such computations. The phase transition temperature between B2 and B19' is estimated to be approximately 500 K for defect-free, single crystals which is about 150 K above experimental results. Defects and

non-equilibrium rate effects are expected to suppress the transition temperature and bring it more into line with experiments.<sup>37</sup> This also suggests opportunities to obtain higher transition temperatures with current materials by improved material processing. A new phase transition in this material is identified between B19' and B33 with an estimated temperature of 75 K. High temperature destabilization of B33 and the corresponding low transition temperature to B19' could explain why B33 has not yet been observed experimentally. Defects could affect this transition as well.

## Methods

Simulations are performed with the Vienna *Ab Initio* Simulation Package (VASP)<sup>38–41</sup> using the frozen core all-electron projector augmented wave (PAW) method<sup>42,43</sup> and the generalized gradient approximation of Perdew, Burke, and Ernzerhof.<sup>44</sup> All DFT-MD simulations employ an energy cutoff of 269.5 eV, an electronic energy convergence criteria of  $1 \times 10^{-7}$  eV, a time step of 3.0 fs, and  $\sim 3000$  k-points per inverse atom. Furthermore, electronic smearing is handled through the Methfessel-Paxton scheme<sup>45</sup> with a smearing width of 0.05 eV, and the computations are not spin polarized. For both Ni and Ti the 3d and 4s electrons are included in the valence. This valence configuration was found to produce free energy results within 1 meV/atom agreement with smaller core simulations that include the 3p in the the Ti valence. Computations are performed on 144 atom supercells, which were found to be free of vibrational size effects. Temperature is controlled through the use of a Langevin thermostat with a simulation-time equivalent friction factor of 100 fs.

For the B33, B19', and B2 phases, structures were optimized at temperature (from 50 to 900 K) to provide negligible stress. Optimization is carried out by performing 3 ps AIMD simulations, obtaining stresses averaged over this period, and altering the cell to decrease the stress. This procedure was iterated until all stresses were  $< 1$  kbar. During the optimization, the value of  $\gamma$  for B19' and B33 was allowed to change to produce negligible shear stress,  $\gamma$  was

held 90° for B2. The value of  $\gamma$  was sensitive to temperature for B19', while it remained near 107.32° for B33. Barrierless, and spontaneous, B33→B19' and B19'→B2 phase transitions were found upon optimization at critical temperatures of 400 K and 800 K, respectively. At and above the critical temperature, geometry optimization was performed with  $\gamma$  for B33 and B19' being held to the terminal values of 107.32° and 97°, respectively.

Zero-temperature phonon dispersions were obtained from the frozen phonon approach using displacements of 0.01 Å. Temperature dependent phonons were computed by fitting force data from 50 ps DFT-MD simulations to a force constant matrix.<sup>33,34</sup> The force constant matrix was then symmetrized in accordance with the crystal structure. Imaginary frequencies were indicated with negative numbers.

Helmholtz free energy computations were provided by a generalized stress-strain method and through a modified Einstein crystal approach. The generalized stress-strain method involves the incremental interpolation of lattice vectors and atomic positions between stress optimized B33 and B19' structures as well as between stress optimized B19' and B2 structures. The resulting path is effectively  $\gamma$ -dependent. The transition between the phases is represented by changes in the tensor composed of the cell lattice vectors,  $\Omega(\lambda)$ , where  $\lambda$  is a mixing parameter that describes a linear change between the initial and final lattice vectors. The initial and final structures correspond to  $\lambda$  values of 0 and 1, respectively, and AIMD simulations were performed on structures at nine intermediate values of  $\lambda$ . The Helmholtz free energy difference between the initial and final structures was then obtained by

$$\Delta F = \int_0^1 V_\lambda \left[ (\sigma \Omega^{-T}) : \frac{\partial \Omega}{\partial \lambda} \right] d\lambda, \quad (1)$$

where  $\sigma$  is the stress tensor and  $V_\lambda$  is the  $\lambda$ -dependent volume. Derivation and validation of this expression is presented in the supplementary material. Extensive convergence tests were performed with respect to simulation parameters and system size (see Supplementary Fig. S10) to ensure accurate measures of free energy.

Checks of the generalized stress strain approach were conducted using the Einstein crystal approach for structures representing free energy minima. The temperature-dependent force constant matrix was employed as a reference harmonic state for which the free energy was known. Thermodynamic integration was then performed between the force constant reference and DFT to provide the anharmonic contribution to free energy. The free energy difference between the reference potential and DFT is given by  $\Delta F = \int_0^1 \langle \frac{\partial U}{\partial \lambda} \rangle_\lambda d\lambda$ . In this expression  $U = U^H - \lambda(U^H - U^{DFT})$ , where  $U^H$  is the harmonic reference potential energy and  $U^{DFT}$  represent the DFT potential energy. The mixing parameter,  $\lambda$ , defines a linear change between the harmonic potential and DFT. MD simulations are performed for potential energy surfaces resulting from  $\lambda$  values of 0, 0.25, 0.5, 0.75, and 1 to produce a smoothly varying  $\partial U / \partial \lambda$ . Convergence tests (see Supplementary Figs. S11 and S12) were performed to ensure accurate measures of free energy.

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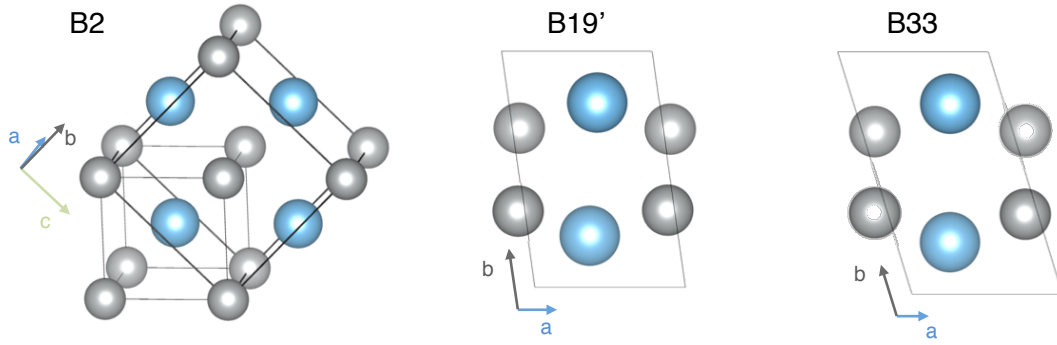


Figure 1: Phases of NiTi including B2 in its primitive, 2 atom cell as well as in a four atom cell that is analogous to the primitive cells of B19' and B33. The monoclinic angle,  $\gamma$ , is defined to be between the  $a$  and  $b$  lattice vectors.

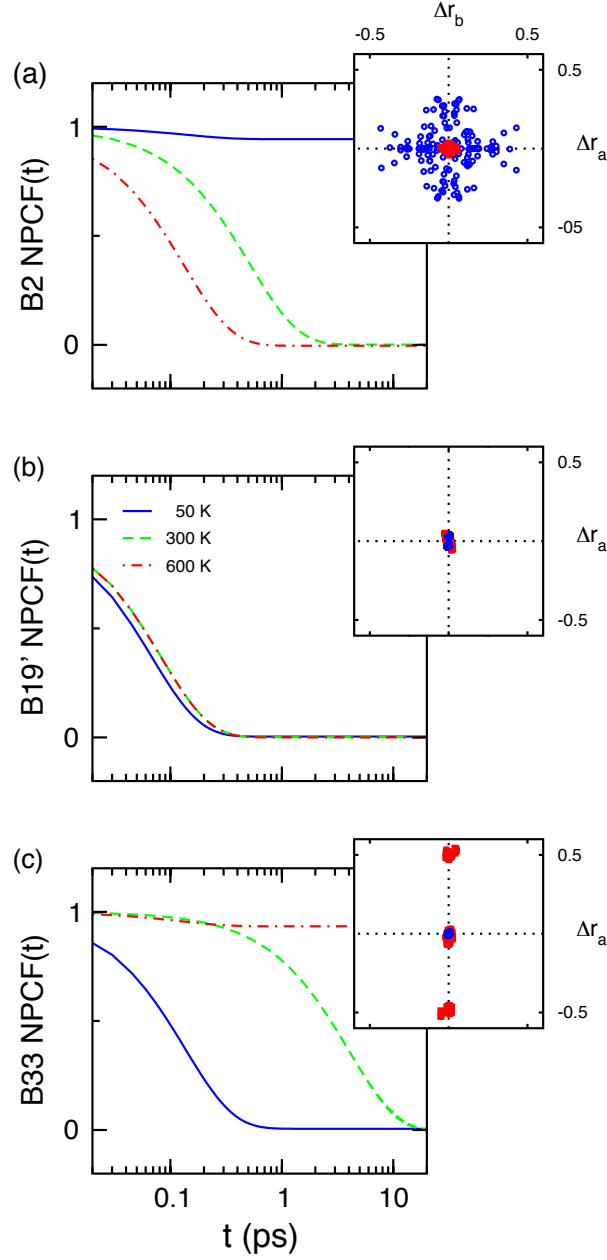


Figure 2: Normalized position correlation function (NPCF) and scatter plots of average atomic displacements from ideal positions along the  $a$  ( $\Delta r_a$ ) and  $b$  ( $\Delta r_b$ ) lattice vectors for (a) B2, (b) B19', and (c) B33. The NPCFs are given for the 144 supercell at 50, 300, and 600 K and differentiate between stable (NPCF( $\infty$ )  $\sim$  0) and unstable (NPCF( $\infty$ )  $\sim$  1) structures. For all cells, scatter plots are given for the lowest tested temperature of 50 K (blue circles) and 600 K (red squares).

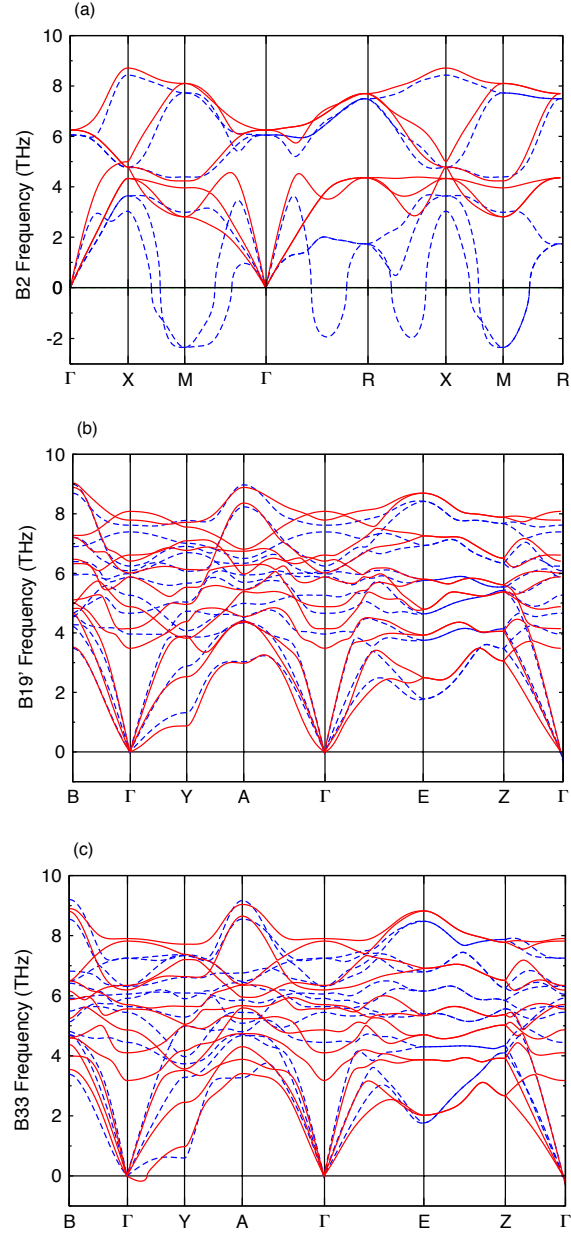


Figure 3: Phonons of the (a) B2, (b) B19', and (c) B33 phases of NiTi at 0 K (blue, dashed line) and 600 K (red, solid line). Temperature-dependent phonons are extracted from simulations using the 144 atom supercell.

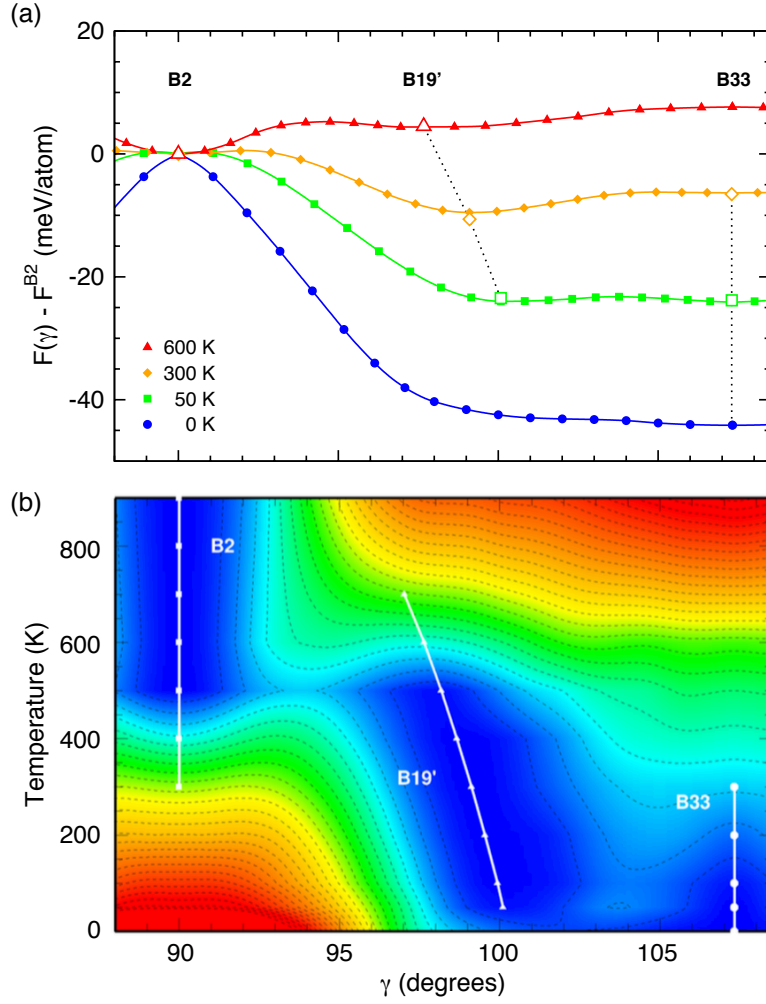


Figure 4: Helmholtz free energy along the  $\gamma$  reaction coordinate as a function of temperature. (a) The free energy profile along the  $\gamma$  reaction coordinate for 0, 50, 300, and 600 K. Filled symbols and lines are obtained through the generalized stress-strain method, while open symbols are provided for free energy minima using the Einstein crystal approach. Error bars for the Einstein crystal method are  $< 1$  meV/atom and not visible at the present scale. (b) Free energy color map as a function of temperature and  $\gamma$ . Regions of low free energy are given as blue, while regions of high free energy are given as red. White lines describe stability basins and also indicates the temperature dependence for the B19' monoclinic angle.

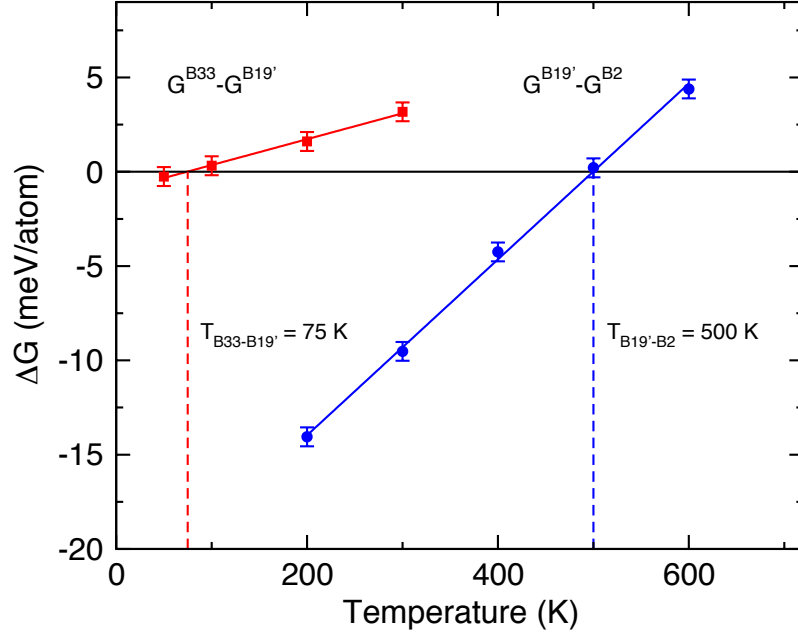


Figure 5: Gibbs free energy differences between B33 and B19' (squares) as well as between B19' and B2 (circles) phases as a function of temperature. Interpolated transition temperatures are indicated with dashed lines. Error bars reflect the 1 meV/atom accuracy of the computations.

## SUPPLEMENTAL MATERIAL

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## 1. ENERGY AND STRUCTURE

Table S1 summarizes a large number of previous  $T = 0$  DFT calculations [1–18] obtained for a range of DFT codes and DFT parameters. These results were assembled for B19', as well as for B19'' and B33 where available. A weakly stable phase (B19'') has been reported recently which is a monoclinic structure very similar to B19', except with a larger monoclinic angle (around  $102^\circ$  instead of  $98^\circ$ ). The existence of B19'' is somewhat controversial with assertions that it may be a computational artifact. The table also reports if a non-zero shear stress was obtained for the B19' cell at a fixed monoclinic angle. While B19' is often found to be unstable, the exceptions are for calculations with small valences or where the valence was not explicitly indicated. Our calculations indicate a similar trend where including  $p$  and  $s$  electrons in the valence destabilizes B19'. We have found that when a calculation is sufficiently converged with respect to smearing value and k-point mesh, B19'' is destabilized, though weakly so. At  $T = 0$  K, we find only B33 to be stable with respect to phonons and cell stresses.

Table S2 shows experimental formation energies [19–22] of B2 as well as the calculated formation energies [1–3, 13, 16, 23–25] of B2, B19', B19'', and B33. The present B2 formation energies are within the range of experimental uncertainty and in good agreement with the values of Hatcher, [3] which were calculated with an all-electron method. The formation energies of B19' and B33 calculated by Hatcher are 14-15 meV/atom lower in energy than the present Ni Ti<sub>pv</sub> calculations.

The varied results shown in Table S1 and Table S2 clearly show that convergence criteria must be studied carefully for this material. We examined the effect on the energetic landscape caused by various calculation convergence parameters. Figures S1



and S2 show the lowest energy structures (referenced to B2) for a range of  $\gamma$  from  $99^\circ$  to  $107.5^\circ$  (approximately B33) with different calculation parameters. PAW potentials with different core/valence configurations are shown in Figure S1 for 16380 k-points per inverse atom and an electron smearing width of 0.05 eV. The Ni Ti potential deviates from the potentials with more valence electrons (up to 6.1 meV/atom compared to Ni<sub>pv</sub> Ti<sub>sv</sub>). The other potentials are all within 1.3 meV/atom of one other. The Ni Ti potential is also differentiated from the others in that it yields a stable B19'' phase while the others yield no energy minima aside from B33. This result parallels the calculations shown in Table S1 where the potentials with the smaller valences produced phases that were not stable when calculated with larger valences.

In Figure S2, we show a similar set of calculations, but instead of changing the valence electrons, the k-point mesh and electron smearing parameter, sigma, are varied. We found that B19'' was stable for larger smearing parameters and less dense meshes, but exploring denser meshes (up to 116,000 k-points per inverse atom) with smaller sigma values (0.01 eV) yielded no stable B19'' phase. For the PBE PAW potentials included with VASP, our convergence tests show that B19' is not a T=0 K energy minima, and B19'' is only a minima for the smallest valence PAW calculations. When these two phases are found with VASP PAW potentials, it is likely because of loose convergence.

In Table S3, the  $T = 0$  K lattice parameters for the 4-atom unit cells of B2, B19', and B33 are shown. As B19' is not a stable minimum on the zero temperature energy profile, the shown parameters are obtained from fixing the angle to  $98.0^\circ$ . The zero-temperature structures have been employed [4, 5] to comment on possible transition paths between the various phases. Most notably, the large  $b$  lattice parameter of

B33, 4.923 Å, is much larger than that of the other phases. There are transition paths that include B33 as an intermediate; however, such paths would lead to large variations in  $b$  that would be unfavorable.

## 2. FINITE TEMPERATURE OPTIMIZATION

The free energy of the B33, B19', and B2 phases were optimized with respect to lattice parameters at temperature to produce structures having negligible stress. The optimization scheme is iterative and entails performing 3 ps DFT-MD simulations, obtaining stresses averaged over this period, and altering the cell according to  $\Omega^{k+1} = \Omega^k - \alpha \frac{\partial F}{\partial \Omega}$ , where  $\Omega$  is a tensor describing the cell shape,  $F$  is the Helmholtz free energy, “ $k$ ” is an iteration index, and  $\alpha$  is a constant parameter. For a generalized crystal,  $\Omega$  is given by

$$(1) \quad \Omega = \begin{bmatrix} a_x & b_x & c_x \\ a_y & b_y & c_y \\ a_z & b_z & c_z \end{bmatrix},$$

where the lattice vectors are  $\mathbf{a} = (a_x, a_y, a_z)$ ,  $\mathbf{b} = (b_x, b_y, b_z)$ , and  $\mathbf{c} = (c_x, c_y, c_z)$ . This procedure was iterated until all components of  $\sigma$  were  $< 1$  kbar, which is considered here to be stress-free and a free energy minimum.

The value of  $\frac{\partial F}{\partial \Omega}$  can be written as in terms of  $\Omega$  and the stress tensor,  $\sigma$ . The free energy of the system in the canonical ensemble is given by

$$(2) \quad F = -\beta^{-1} \ln(\mathcal{Z}),$$

where  $F$  is the Helmholtz free energy,  $\mathcal{Z}$  is the partition function, and  $\beta^{-1}$  is equal to the product of the Boltzmann constant and temperature. The partition function is given by  $\mathcal{Z} = \int \Pi_{i=1}^N d\mathbf{r}_i d\mathbf{p}_i e^{-\beta\mathcal{H}}$ , where  $\int \Pi_{i=1}^N d\mathbf{r}_i d\mathbf{p}_i \dots$  represents the integral over phase space. The Hamiltonian,  $\mathcal{H}$ , describing this system is

$$(3) \quad \mathcal{H} = \sum_{i=1}^N \frac{\mathbf{p}_i \cdot \mathbf{p}_i}{2m_i} + U(\{\mathbf{r}_i\}),$$

where  $\mathbf{p}_i$  and  $m_i$  are the momentum and mass of particle “i”, the summation in the first term is taken over the  $N$  atoms in the system, and  $U$  is potential energy, which is determined by the set of all atomic positions  $\{\mathbf{r}_i\}$ . The derivative of  $F$  with respect to  $\Omega$  is given by

$$(4) \quad \frac{\partial F}{\partial \Omega} = -\beta^{-1} \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \Omega}.$$

One may expand the derivative of  $\mathcal{Z}$  with respect to  $\Omega$  by performing a canonical transformation on the coordinates  $\mathbf{r}$  and momenta  $\mathbf{p}$ , such that

$$(5) \quad \begin{aligned} \mathbf{r}_i &= \Omega \boldsymbol{\rho}_i \\ \mathbf{p}_i &= \boldsymbol{\pi}_i \Omega^{-1}, \end{aligned}$$

where  $\boldsymbol{\rho}_i$  are reduced coordinates,  $\boldsymbol{\pi}_i$  are transformed momentum, and a superscript “-1” indicates the inverse tensor. This transformation preserves the dynamics derived from the Hamiltonian, and leads to the partition function being written as  $\int \Pi_i d\boldsymbol{\pi}_i d\boldsymbol{\rho}_i e^{-\beta\mathcal{H}(\{\boldsymbol{\pi}_i\}, \{\boldsymbol{\rho}_i\})}$ . The free energy expression in Eq. 4 then reduces to

$$(6) \quad \frac{\partial F}{\partial \Omega} = \left\langle \frac{\partial \mathcal{H}(\{\boldsymbol{\pi}_i\}, \{\boldsymbol{\rho}_i\})}{\partial \Omega} \right\rangle,$$

where  $\langle \dots \rangle$  denotes the ensemble average. The transformed Hamiltonian is given by

$$(7) \quad \mathcal{H} = \sum_{i=1}^N \frac{1}{2m_i} (\boldsymbol{\pi}_i \Omega^{-1}) \cdot (\boldsymbol{\pi}_i \Omega^{-1}) + U(\{\Omega \boldsymbol{\rho}_i\}).$$

The derivative of  $\mathcal{H}$  with respect to  $\Omega$  may then be written as

$$(8) \quad \frac{\partial \mathcal{H}}{\partial \Omega} = \sum_{i=1}^N \frac{1}{m_i} (\boldsymbol{\pi}_i \Omega^{-1}) \cdot \frac{\partial (\boldsymbol{\pi}_i \Omega^{-1})}{\partial \Omega} + \sum_{i=1}^N \frac{\partial U}{\partial (\Omega \boldsymbol{\rho}_i)} \cdot \frac{\partial (\Omega \boldsymbol{\rho}_i)}{\partial \Omega}.$$

Employing vector-matrix manipulations, one may rearrange Eq. 8 as

$$(9) \quad \frac{\partial \mathcal{H}}{\partial \Omega} = - \sum_{i=1}^N \frac{1}{m} (\boldsymbol{\pi}_i \Omega^{-1}) \otimes (\boldsymbol{\pi}_i \Omega^{-1}) \Omega^{-T} - \sum_{i=1}^N \mathbf{f}_i \otimes \boldsymbol{\rho}_i,$$

where  $\mathbf{f}$  is force,  $\otimes$  is the outer product operation, and “ $-T$ ” indicated the transpose of the inverse. Transforming back to  $\mathbf{p}$  and  $\mathbf{r}$  leads to

$$(10) \quad \frac{\partial \mathcal{H}}{\partial \Omega} = - \sum_{i=1}^N \frac{1}{m_i} (\mathbf{p}_i \otimes \mathbf{p}_i) \Omega^{-T} - \sum_{i=1}^N (\mathbf{f}_i \otimes \mathbf{r}_i) \Omega^{-T}.$$

The quantity given by  $-\sum_{i=1}^N \{\frac{1}{m} (\mathbf{p}_i \otimes \mathbf{p}_i) + (\mathbf{f}_i \otimes \mathbf{r}_i)\}$  is the product of the absolute value of the determinant of  $\Omega^T$ , or volume, with the stress tensor,  $|det \Omega^T| \sigma$ . Using these relations with Eq. 6 leads to the final expression for the derivative of free energy,

$$(11) \quad \frac{\partial F}{\partial \Omega} = |det \Omega^T| (\sigma \Omega^{-T}),$$

which may be employed to optimize  $F$  with respect to lattice vectors.

### 3. PHONON DISPERSIONS

In Figure S3, the well known phonon dispersion of the cubic unit cell at  $T = 0$  K of B2 is given as a function of supercell size. The smaller end of the size range,

3x3x3 to 5x5x5 supercells, are given in Figure S3a. Increasing size from 3x3x3 to 5x5x5 reduces the frequency of the imaginary modes. Additionally, there is some minor distortion of low frequency modes in the  $M \rightarrow \Gamma$  direction, near the  $\Gamma$ -point. The 5x5x5 supercell results in imaginary frequencies near the  $\Gamma$ -point. To remove any ambiguity in the discussion of size effects on the B2 phonons, we have computed the phonon dispersions for 6x6x6, 7x7x7, and 8x8x8 supercell. A comparison of the dispersions at these sizes, given in Figure S3b, indicates that size effects are effectively mitigated by using a 6x6x6 or larger supercell. With respect to the smaller sizes, the anomalous imaginary modes near the  $\Gamma$  point vanish at these large sizes, and a fine structure of the imaginary modes along the  $X \rightarrow M$  direction develops.

The  $T = 0$  K phonon dispersions of the monoclinic B19', and B33 phases are given in Figures S4 and S5). As opposed to B2, the unit cell for the monoclinic phases contains 4 atoms. For these systems, phonon dispersions have been computed for 3x2x2, 4x3x3, and 5x4x4 supercells, each of which has similar a, b, and c lattice parameters. For all of these cells, the influence of size is relatively minor, with the acoustic modes along the  $\Gamma \rightarrow E \rightarrow Z$  path exhibiting variations of roughly 1 THz.

The influence of supercell on zero temperature phonon dispersions arises from interactions of images of displaced atoms. In a dynamical system, the number of existing phonon modes is a finite number that is determined by the size of the system. Simulations using larger supercells will have a denser population of phonon modes in reciprocal space. The vibrational properties resulting from such a dynamical simulation must therefore be converged with respect to supercell size.

A more explicit analysis of supercell size effects on the  $T$ -dependent vibrations is through the computation of  $T$ -dependent phonon dispersions. We show such a

dispersions for the 3x3x3 supercell of the 2 atom B2 unit cell at 300, 600, and 900 K in Figure S6. From this size, the imaginary modes centered about the M-point persist up to 600 K. At 900 K, the imaginary modes are not present, and the B2 crystal is assumed stable. The B2 phonon dispersion is also shown for a 6x6x6 supercell in Figure S7. In this case, there are no imaginary modes all the way down to 300 K, suggesting phase stability. These results are in qualitative agreement with our previous analysis of size effects in the  $T = 0$ , and again suggests phase stability is strongly influence by system size in the 3x3x3 unit cell.

Many of our free energy energy computations utilize the 4 atom unit cell for DFT-MD simulations. To complete our analysis of size effects, we provide the stability behavior of the 4x3x3 supercell in terms of  $T$ -dependent phonons in Figure S7. We have chosen a 4x3x3, 144 atom supercell of 4 atom unit cells for our free energy computations. As with the 6x6x6 supercell, the 4x3x3 supercell exhibits stability down to 300 K.

#### 4. FREE ENERGY: GENERALIZED STRESS-STRAIN METHOD

A path between the low temperature monoclinic phases of NiTi, B33 and B19', and the high temperature phase, B2, can be established as a function of the monoclinic angle,  $\gamma$ . This presents a natural path variable for the computation of free energy. The free energy changes resulting from distortion of lattice vectors have been previously described for the limited case of the constant volume bcc $\rightarrow$ fcc Bain path. [26] We here generalize this formalism to treat the variable volume deformation of any cell. Incorporation of variable volume allows for a transformation path between two stable phases at a given temperature but different volumes, which is the case for

NiTi phases of interest. Because the present investigation occurs at zero pressure, the resulting difference in free energy is equivalent to Gibbs free energy.

The  $\Omega$  tensor can be continuously deformed from the low temperature monoclinic phases to the high temperature B2 phase. This deformation can be effected by defining  $\Omega$  to be dependent on a mixing parameter,  $\lambda$ , that linearly changes  $\Omega$  from an initial state to a final state, or  $\Omega(\lambda) = \Omega^0 - \lambda(\Omega^0 - \Omega^1)$ . The values of  $\Omega$  at  $\lambda = 0$  and 1 correspond to structures of stable phases,  $\Omega^0$  and  $\Omega^1$ , respectively. Through the use of Eq. 4, the free energy change upon such a deformation may be represented as

$$(12) \quad \Delta F = -\beta^{-1} \int_0^1 \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \lambda} d\lambda = -\beta^{-1} \int_0^1 \frac{1}{\mathcal{Z}} \frac{\partial \mathcal{Z}}{\partial \Omega} : \frac{\partial \Omega}{\partial \lambda} d\lambda,$$

where  $\frac{\mathcal{Z}}{\partial \Omega}$  and  $\frac{\partial \Omega}{\partial \lambda}$  are both tensors and “:” denotes the Frobenius inner product (*i.e.*,  $\sum_{ij} \frac{\partial \mathcal{Z}}{\partial \Omega_{ij}} \frac{\partial \Omega_{ij}}{\partial \lambda}$ ). The changes in Helmholtz free energy given by Eq. 12 do not require a constant volume. When the integration is performed between zero-pressure states, as in the present work, the resulting measure of free energy is equivalent to Gibbs free energy. The free energy expression in Eq. 12 further reduces to

$$(13) \quad \Delta F = \int_0^1 \left\langle \frac{\partial \mathcal{H}(\boldsymbol{\pi}, \boldsymbol{\rho})}{\partial \Omega} \right\rangle : \frac{\partial \Omega}{\partial \lambda} d\lambda.$$

Using Eq. 10 with Eq. 13 leads to the final expression for free energy,

$$(14) \quad \Delta F = \int_0^1 V_\lambda \left[ (\sigma \Omega^{-T}) : \frac{\partial \Omega}{\partial \lambda} \right] d\lambda,$$

where  $V_\lambda$  is defined as  $|\det \Omega^T|$ .

For NiTi, the lattice vectors of both the low-temperature martensite B33 and B19' structures as well as the high-temperature B2 structure can be represented as

a tensor  $\Omega$ , given by

$$(15) \quad \Omega = \begin{bmatrix} a_x & b_x & 0 \\ 0 & b_y & 0 \\ 0 & 0 & c_z \end{bmatrix}.$$

Using this with Eq. 11 leads to

$$(16) \quad \Delta F = \int_0^1 V_\lambda \left\{ \sigma_{xx} \frac{\partial \ln a_x}{\partial \lambda} + \sigma_{yy} \frac{\partial \ln b_y}{\partial \lambda} + \sigma_{zz} \frac{\partial \ln c_z}{\partial \lambda} - \sigma_{xy} \frac{b_x}{b_y} \left[ \frac{\partial \ln a_x}{\partial \lambda} - \frac{\partial \ln b_x}{\partial \lambda} \right] \right\} d\lambda.$$

The stresses in this formulation are obtained from DFT-MD simulations, which must be suitably long to provide a well-converged measure of stress. The time averages of stress components required for Eq. 16 are given in Figure S8. Stresses are given for the B2 ( $\lambda = 0$ ) and B19' ( $\lambda = 1$ ) phases, as well as for an interpolated structure between these phases ( $\lambda = 0.5$ ). In all cases, the stresses converge in a well-behaved manner and reach full convergence, which is defined to be within 1 kbar of the long-time average, within a few picoseconds. As a standard practice in the present work, we employ 10 ps DFT-MD simulations for points along our stress strain  $\lambda$  path.

The numerical accuracy of the DFT techniques could influence the average stress obtained from MD simulations, as well as the resulting measure of free energy. Free energy profiles along  $\lambda$  for various levels of numerical accuracy are presented in Figure S9. For each numerical configuration, the structure of B2 and B19', which correspond to  $\lambda$  values of 0 and 1, respectively, have been fully optimized. DFT-MD simulations are performed for nine structures (a  $\lambda$  spacing of 0.1) obtained by linearly interpolating between B2 and B19',  $B2 - \lambda(B2 - B19')$ . Our default simulation parameters correspond to the Ni Ti<sub>pv</sub> pseudo potential, a 6x5x6 k-point mesh, a 269.5 eV



energy cutoff, and a energetic convergence criteria of  $10^{-7}$ . To evaluate the tolerance of free energy to these parameters, we have performed single substitutions of each parameter and recomputed the free energy profile. Employing the large Ni Ti core results in variations along the  $\lambda$  path but no significant change in  $F(1) - F(0)$ . For k-points, both 4x4x4 and 7x7x7 k-point meshes have been employed. Both meshes result in slightly higher transition barriers, though the difference between B19' and B2 free energies agrees with that obtained from simulations with the default parameters. For the energy cutoff. As with the other parameters, the energy cutoff, too, results in the same free energy differences between the stable phases as the default parameters. The free energy difference is a weak function of the above parameters. More accurate methods, including smaller cores and more accurate functionals, are not tenable to DFT-MD simulations, but could very well have a marked influence on free energy.

As a final note, the free energy profile for the generalized stress-strain method represents a single interpolated path between two phases in lattice vector configuration space. This implies that the free energy barriers are likely upper bounds to an alternative path exhibiting lower stress. Nevertheless, the path chosen for the present work coincides with motion along the  $[100](011)$  generalized stacking fault, which is meaningful as it has been experimentally conjectured as a possible physical path for transition. The changes in atomic configuration along this path are well-behaved and reversible and the resulting free energy agrees well with Einstein crystal approaches, as described in the next section. The above evidence suggests that errors resulting from loss of lattice stability along the path or from constrained cell effects [27, 28] are minimal.

## 5. FREE ENERGY: EINSTEIN CRYSTAL METHODS

One may additionally use the principles of thermodynamic integration.

$$(17) \quad \Delta F = \int_0^1 \left\langle \frac{\partial U}{\partial \lambda} \right\rangle_{\lambda=\lambda'} d\lambda'$$

The potential energy is taken from a reference system, which preferably has a known value of free energy, to the system of interest, given as  $U = U^{ref} - \lambda(U^{ref} - U^{full})$ . Choices for  $U^{ref}$  have ranged from single harmonic wells to full force constant matrix to represent the internal energy of the crystal. The spring constant is a generally poor choice for  $U^{ref}$ , while the force constant matrix is sensible if the crystal is stable and phonons are real. There are a few classes of systems where application can vary: disordered systems, ordered crystal with unstable phonons, and ordered crystals with stable phonons.

In essence, the choice of reference potential will vary with respect to system type. For the first case of a highly disordered solid system, the spring constant approach may be a sensible reference potential. For ordered crystalline systems, phonons are an excellent choice for reference potential. For ordered systems with unstable modes at  $T = 0$  K, the stabilized T-dependent phonons are used as a reference potential. The convergence of  $U$  with respect to  $\lambda$  for all phases at 300 K is given in Figure S10. For all phases, the derivatives are shown to converge within 10 ps. Profiles of  $\frac{\partial U}{\partial \lambda}$  as a function of  $\lambda$  are shown in Figure. S11. The highly harmonic nature of B33 and B19' are exhibited in the minor variation in  $\frac{\partial U}{\partial \lambda}$  over the  $\lambda$  range. The large variation of  $\frac{\partial U}{\partial \lambda}$  for B2 may be attributed to its highly anharmonic character.

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TABLE S1. Survey of literature results for the relative energies of B19', B19'' and B33 with respect to B2 for different DFT codes and DFT parameters.

	Program	Method	XC	Valence	Spin	E-E <sup>B2</sup> (meV/atom)			
						B19'	Stable?	B19''	B33
OQMD [1]	VASP	PAW	PBE	Ni Ti	yes	-31.0	yes(98.3)		
Materials Project [2]	VASP	PAW	PBE	Ni <sub>pv</sub> Ti <sub>pv</sub>	yes			-54.2	
Hatcher [3–5]		FLAPW	PBE	All electron	no	-56.0	no		-60.1
Vishnu [6]	SeqQuest	LCAO NC PP	PBE	Ni Ti <sub>pv</sub>	no	-40.5	no	-43.5	-46.0
Vishnu [6]	SeqQuest	LCAO NC PP	PBE	Ni Ti	no	-40.5	yes	-46.5	-48.5
Wagner [7]	VASP	PAW	PW91	Ni Ti <sub>pv</sub>	yes	-44.0	no		-49.5
J. Wang [8]	VASP	PAW	PW91		no	-44.1	yes	-51.4	-52.4
Huang [9]	VASP	USPP	LDA	Ni Ti <sub>pv</sub>	yes	-49.0	no		-54.0
Huang [9]	VASP	PAW	LDA	Ni Ti <sub>pv</sub>	yes				-54.0
Huang [9]	VASP	USPP	PW91	Ni Ti <sub>pv</sub>	yes	-42.0	no		-50.0
Holec [10]	VASP	PAW	PBE		no	-33.5	yes(95.3)	-41.5	-42.0
Kibey [11]	VASP	PAW	PW91		no	-39.5	yes		
Sestak [12]	VASP	PAW	PW91	Ni Ti <sub>pv</sub>	no	-40.3	no		-48.0
Sestak [12]	ABINIT	NC PP	PBE	Ni Ti	no	-13.6	no		-66.4
Pasturel [13]		LMTO-ASA	LDA	All electron	no	-17.6	yes (96.8)		
Pasturel [13]		FP-LMTO	LDA	All electron	no	-18.7	yes (96.8)		
Parlinski [14]	VASP	USPP	GGA	Ni Ti	no	-43.0	yes		
X. Wang [15]	VASP	PP	LDA		no	-51.0	yes		
Ye [16]		NC PP	LDA		no	-45.0	yes		
Zeng [17]	VASP	PAW	PBE	Ni <sub>pv</sub> Ti <sub>pv</sub>	no	-42.9	yes		-44.7
This work	VASP	PAW	PBE	Ni Ti	yes	-39.6	no	-41.2	-41.6
This work	VASP	PAW	PBE	Ni Ti <sub>pv</sub>	yes	-38.2	no		-41.5
This work	VASP	PAW	PBE	Ni <sub>pv</sub> Ti <sub>pv</sub>	yes	-40.6	no		-44.2
This work	VASP	PAW	PBE	Ni Ti <sub>sv</sub>	yes	-38.4	no		-41.7
This work	VASP	PAW	PBE	Ni <sub>pv</sub> Ti <sub>sv</sub>	yes	-40.8	no		-44.5
Mutter [18]		EAM				-54.0	yes		

LCAO: Linear Combination of Atomic Orbitals

NC: Norm Conserving

PP: Pseudopotentials

PAW: Projector Augmented Waves

EAM: Embedded Atom Method

FLAPW: Full Potential Linearized Augmented Plane Wave Method

USPP: Ultrasoft Pseudopotential

LMTO-ASA: Linear Muffin Tin Orbital-Atomic Sphere Approximation

FP-LMTO: Full Potential-Linear Muffin Tin Orbital

Ni: 3d9 4s1

Ni<sub>pv</sub>: 3p6 3d8 4s2

Ti: 3d3 4s1

Ti<sub>pv</sub>: 3p6 3d3 4s1

Ti<sub>sv</sub>: 3s2 3p6 3d3 4s1

TABLE S2. Formation energies of NiTi phases.

						$E^{form}$ (eV/atom)				
Experimental Method						B2	B19'	Stable?	B19''	B33
Hu [19]	Direct reaction calorimetry					-0.3742				
Kubaschewski [20]	Direct reaction calorimetry					-0.3513				
Gachon [21]	Direct reaction calorimetry					-0.3524				
Guo [22]	Direct reaction calorimetry					-0.3431				
	Program	DFT Method	XC	Valence	Spin	B2	B19'	Stable?	B19''	B33
OQMD [1]	VASP	PAW	PBE	Ni Ti	yes	-0.378	-0.409	yes(98.3)		
Materials Project [2]	VASP	PAW	PBE	Ni <sub>pv</sub> Ti <sub>pv</sub>	yes	-0.3437			-0.3979	
Hatcher [3–5]		FLAPW	PBE	All electron	no	-0.353	-0.409	no		-0.4135
Pasturel [13]		LMTO-ASA	LDA	All electron	no	-0.3949	-0.4125	yes (96.8)		
Pasturel [13]		FP-LMTO	LDA	All electron	no	-0.3731	-0.3918	yes (96.8)		
Lu [23]		EMTO-CPA	PBE	Ni Ti	no	-0.34				
Douglas [24]	VASP	PAW	PBE		yes	-0.411				
Tokunaga [25]		FLAPW	GGA	All electron	no	-0.3585				
Ye [16]		NC PP	LDA		no	-0.66	-0.705	yes		
This work	VASP	PAW	PBE	Ni Ti	yes	-0.3439	-0.3835	no	-0.3851	-0.3855
This work	VASP	PAW	PBE	Ni Ti <sub>pv</sub>	yes	-0.3574	-0.3955			-0.3989
This work	VASP	PAW	PBE	Ni <sub>pv</sub> Ti <sub>pv</sub>	yes	-0.3555	-0.3961	no		-0.3997
This work	VASP	PAW	PBE	Ni Ti <sub>sv</sub>	yes	-0.3574	-0.3958	no		-0.3991
This work	VASP	PAW	PBE	Ni <sub>pv</sub> Ti <sub>sv</sub>	yes	-0.3557	-0.3965	no		-0.4002
PAW: Projector Augmented Waves						Ni: 3d9 4s1				
FLAPW: Full Potential Linearized Augmented Plane Wave Method						Ni <sub>pv</sub> : 3p6 3d8 4s2				
LMTO-ASA: Linear Muffin Tin Orbital-Atomic Sphere Approximation						Ti: 3d3 4s1				
FP-LMTO: Full Potenital-Linear Muffin Tin Orbital						Ti <sub>pv</sub> : 3p6 3d3 4s1				
EMTO-CPA: Exact Muffin Tin Orbitals-Coherent Potential Approximation						Ti <sub>sv</sub> : 3s2 3p6 3d3 4s1				
PAW: Projector Augmented Waves										
NC PP: Norm Conserving Pseudopotentials										

TABLE S3. Structure of T = 0 K phases of NiTi.

Phase	Group	a	b	c	$\gamma$	V
B2	$Pm\bar{3}m$	3.007	4.260	4.260	90.00	13.67
B19'	$P2_1/m$	2.922	4.676	4.058	98.00 <sup>†</sup>	13.72
B33	$Cmcm$	2.925	4.923	4.015	107.32	13.80

<sup>†</sup>angle fixed



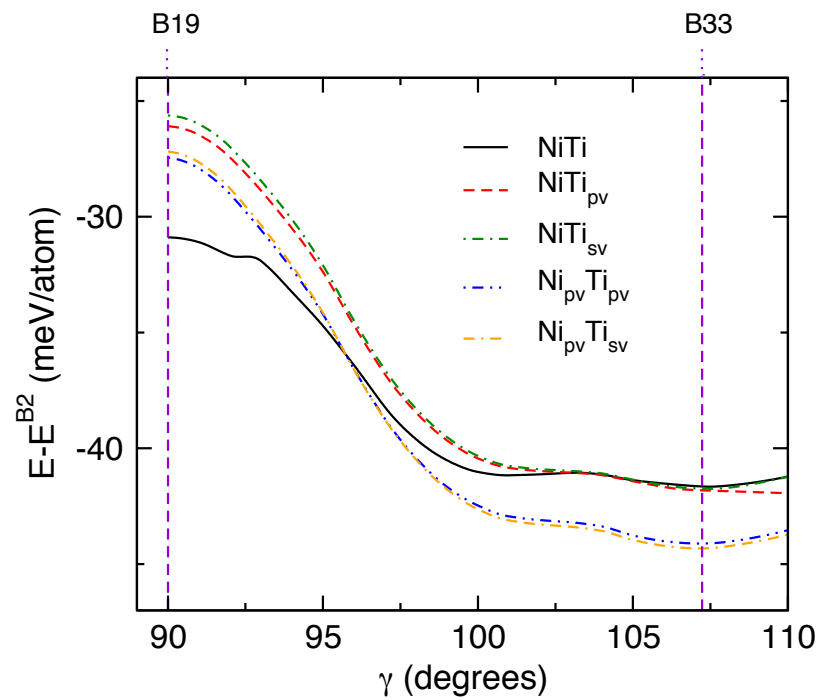


FIGURE S1. Energy of NiTi versus monoclinic angle,  $\gamma$ , for different pseudopotential core size.

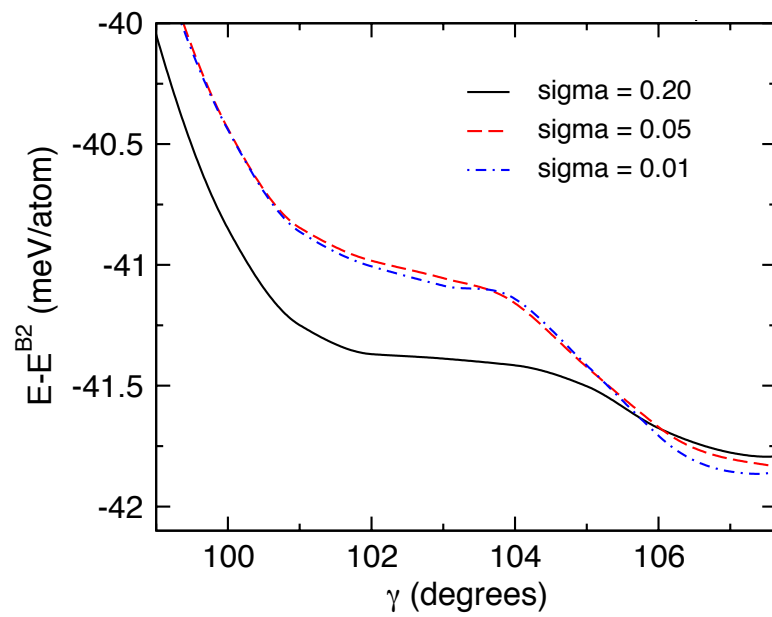


FIGURE S2. Energy of NiTi versus monoclinic angle,  $\gamma$ , for different electron smearing width,  $\sigma$ .

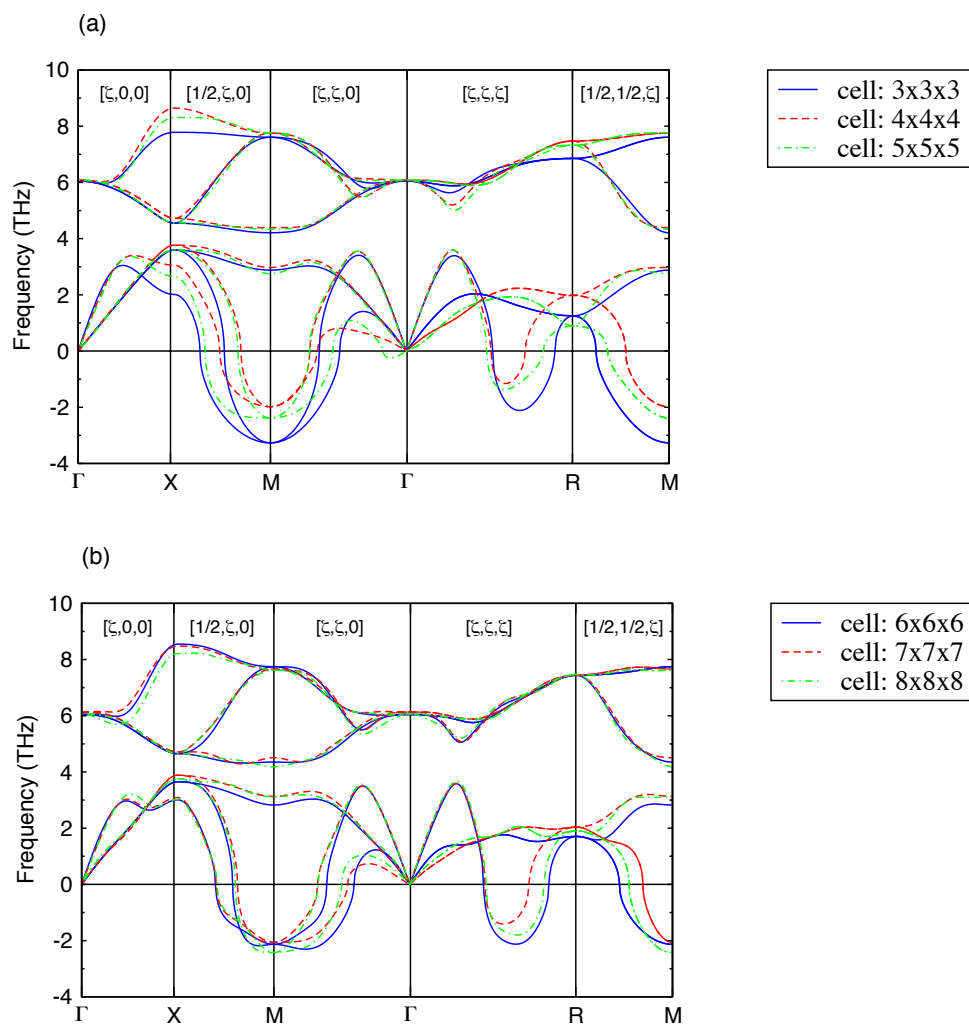


FIGURE S3. Phonon dispersion of cubic B2 NiTi for 3x3x3 to 8x8x8 supercells.

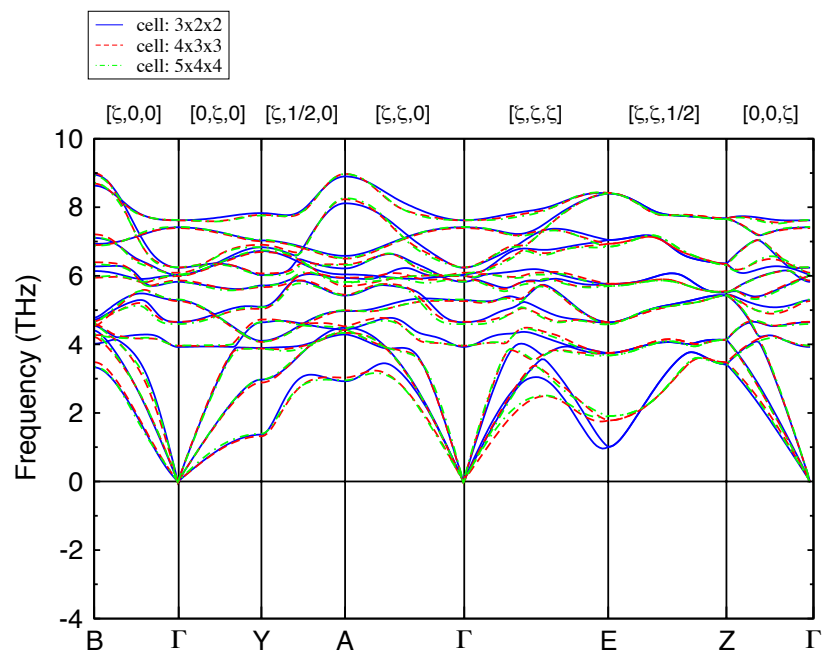


FIGURE S4. Phonon dispersion of B19' NiTi for 3x2x2, 4x3x3, 5x4x4 supercells.

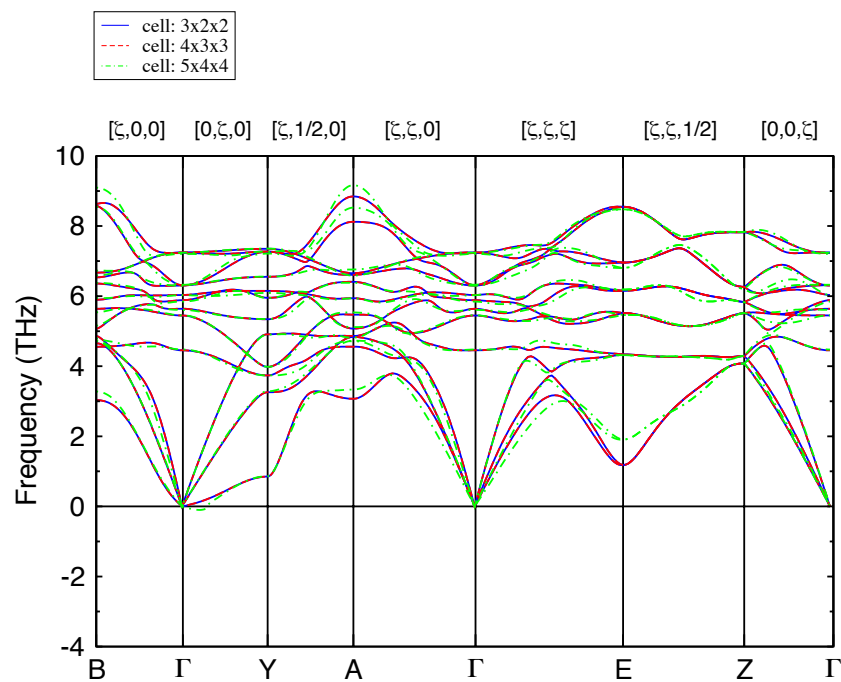


FIGURE S5. Phonon dispersion of B33 NiTi for 3x2x2, 4x3x3, 5x4x4 supercells.

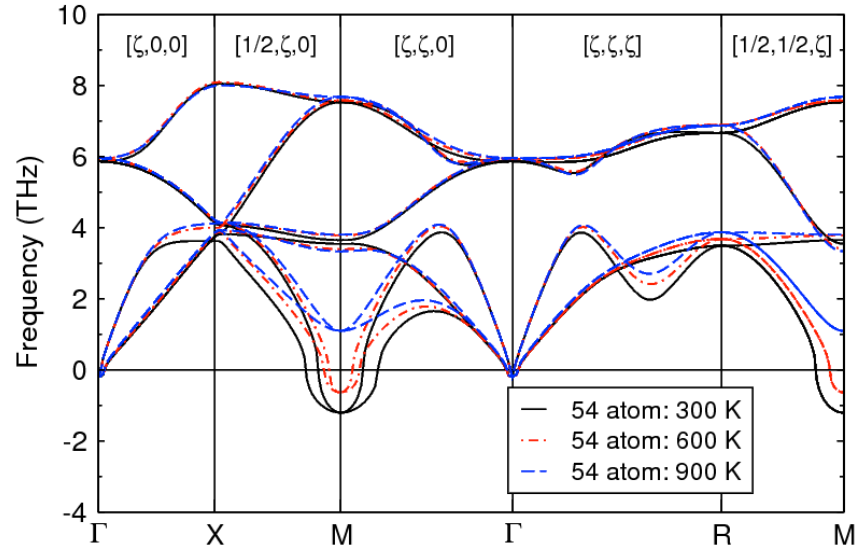


FIGURE S6. Phonon dispersion of a 3x3x3 supercell of B2 NiTi at 300, 600 and 900 K.

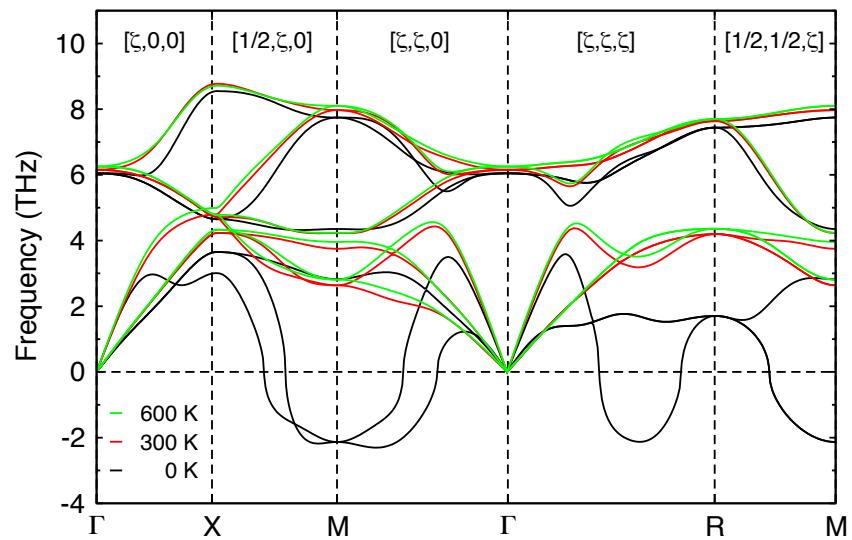


FIGURE S7. Phonon dispersion of a 6x6x6 supercell of B2 NiTi at 0, 300, and 600 K.

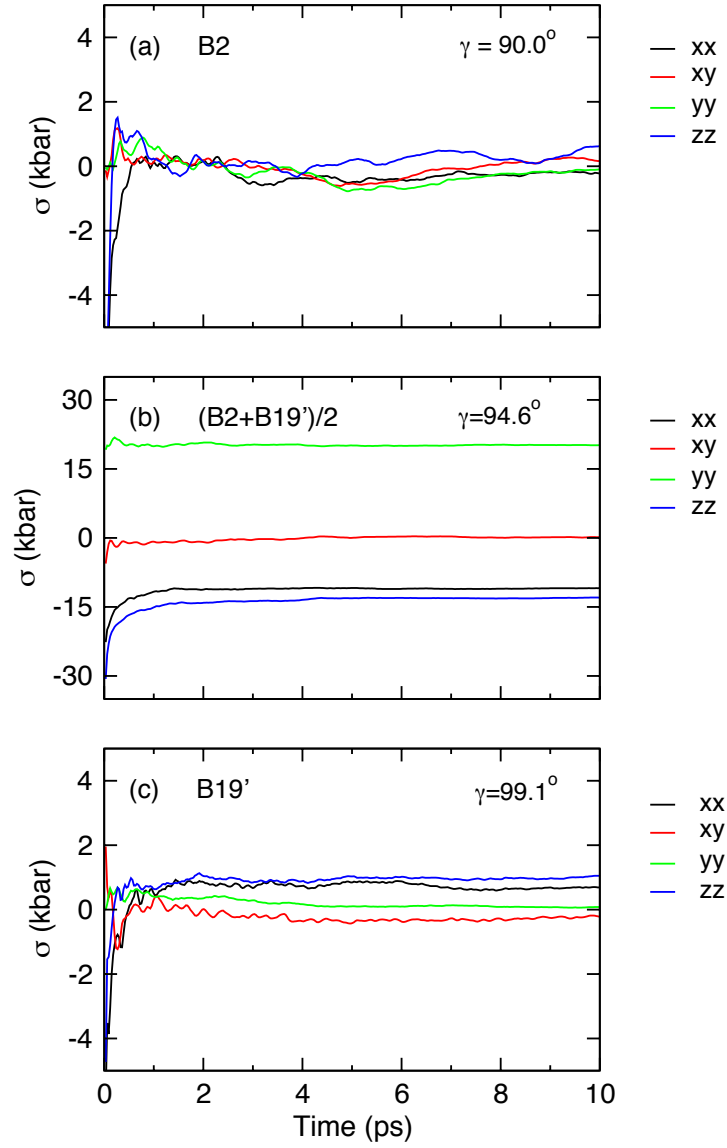


FIGURE S8. Convergence of (a) B2, (b) the interpolated structure half-way between B2 and B19', and (c) B19' stress components employed for free energy with respect to simulation time at 300 K for 4x3x3 supercells.



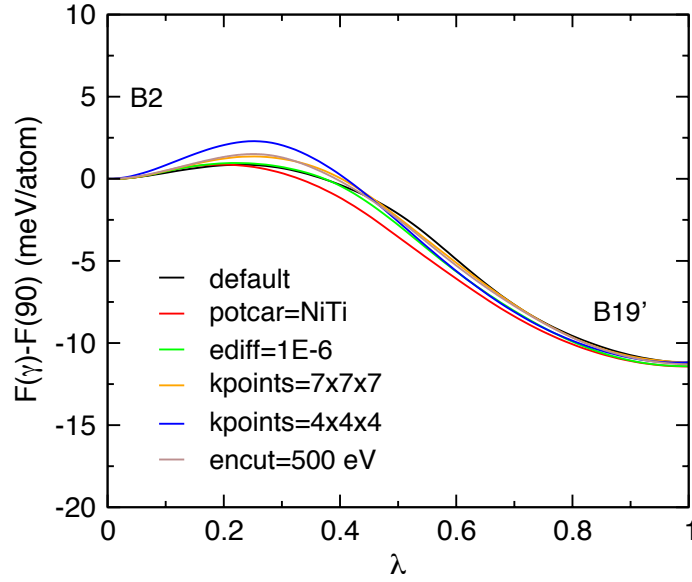


FIGURE S9. Free energy as a function of  $\gamma$  between B2 and B19' as determined by the stress-strain method for various levels of numerical accuracy. Results are shown for a 3x2x2 supercell having 48 atoms at 300 K. The VASP specific term potcar, ediff, and encut refer to the employed pseudopotential, the electronic energy convergence criteria, and the cutoff energy for the plane wave basis set.

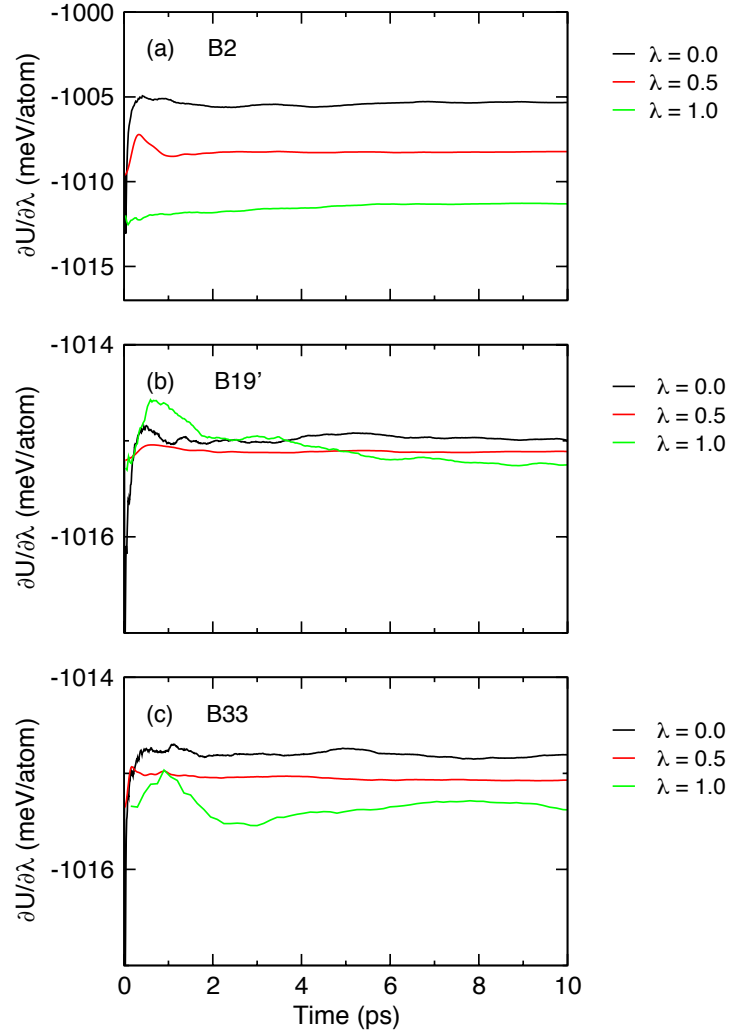


FIGURE S10. Convergence of  $\langle \partial U / \partial \lambda \rangle$  at 300 K as a function of simulation time of (a) B2, (b) B19', and (c) B33. The derivative is given for constant  $\lambda$  values of 0.0, 0.5, and 1.0.

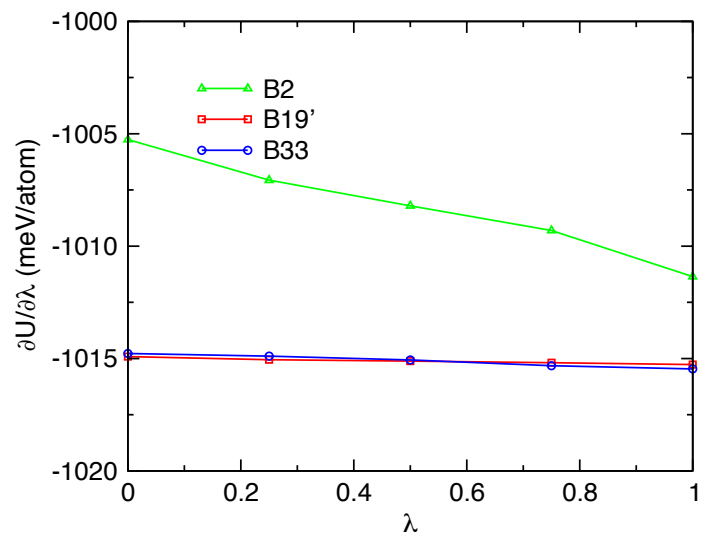


FIGURE S11. Profile of  $\langle \partial U / \partial \lambda \rangle$  at 300 K as a function of  $\lambda$  for B2, B19', and B33. Results are shown for 300 K and a 4x3x3, 144 atom supercell.